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INFLUENCE OF TEMPERATURE ON THE PYROLYSIS OF CALCIUM
CARBONATE IN AN ISOTHERMAL CONTAINER IN A STREAM OF
NITROGEN OR UNDER CONSTANT VACUUM

Jean-Paul Auffredic and Pierre Vallet

Translation of "Influence de la température sur la
pyrolyse du carbonate de calcium, en enceinte
isotherme, dans un courant d'azote ou sous
vide entretenu."

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INFLUENCE OF TEMPERATURE ON THE PYROLYSIS OF CALCIUM
CARBONATE IN AN ISOTHERMAL CONTAINER IN A STREAM OF
NITROGEN OR UNDER CONSTANT VACUUM

J. P. Auffredic and P. Vallet

ABSTRACT: Pyrolysis of a block of calcium carbonate is studied. Pyrolyses were carried out in a stream of nitrogen and under constant vacuum. Expressions are developed for the reaction rate constants, and the activation energy is determined. Pyrolysis is much more rapid under constant vacuum than in the stream of nitrogen.

In a recent study [1, 2, 3], we showed experimentally that in an isothermal vessel, the pyrolysis of a block of calcium carbonate carried out in a stream of nitrogen or under constant vacuum obeys, as a function of time t , a general law of the type

$$1 - \sqrt[3]{x} = \alpha t + \beta t^2 + \gamma t^3, \quad (1)$$

where $x = m/m_0$ represents the fraction of undecomposed matter at instant t , m being the mass of undecomposed carbonate at instant t and m_0 its initial mass.

However, pyrolyses carried out under constant vacuum obey even more perfectly the law (1) supplemented with two terms

$$1 - \sqrt[3]{x} = \alpha t + \beta t^2 + \gamma t^3 + \delta t^4 + \eta t^5, \quad (2)$$

where β and δ are negative.

Similarly, we have shown that the decomposition temperature θ at different points of a cube of marble reached by the decomposition at instant t follows the law

$$\theta = A + Bt + Ct^2. \quad (3)$$

In equations (1), (2) and (3), the coefficients α , β , γ , δ , η , A , B and C are constant for a given cube at a given temperature of the reaction vessel.

We studied the influence of the absolute temperature T_0 of the isothermal vessel on these different coefficients, the final decomposition time t_f and the initial velocity v_0 on the pyrolysis. The mode of operation was the same as in

* Numbers in the margin indicate pagination in the foreign text.

our previous studies [1, 2]. We used cubes of white marble of initial mass $m_0 = 18.434$ g and initial side $2 a_0 = 19.05$ mm. The different cubes were heated in the reaction vessel to temperatures ranging from 740 to 895°C.

1. Pyrolyses carried out in a stream of nitrogen Let y_i be any of the quantities t_F , v_0 , α , $|\beta|$, γ , A , $|B|$ or C and the index i designate the rank (from 1 to 8) of the quantity in this enumeration. They all obey the same general law

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$$\log y_i = a_i T_0^{-1} + \log b_i \quad (4)$$

or

$$y_i = b_i e^{\frac{a_i \ln 10}{T_0}}, \quad (5)$$

in which a_i and $\log b_i$ are constants. In the case of v_0 , we obtain the Arrhenius law, where E is the activation energy, $E = R a_i \ln 10 = 4.576 a_i$ (cal), R designating the constant of perfect gases.

Table I gives the different values of a_i and $\log b_i$ calculated by the least squares method, r_i being the coefficient of linear correlation between $\log y_i$ and T_0^{-1} , I_{a_i} and $I_{\log b_i}$ respectively, the confidence intervals are at a probability threshold of 0.05 of a_i and $\log b_i$; $I_{\log y_i}$ designates the confidence interval which $\log y_i$ is calculable by means of equation (4) at the same probability threshold. The following conclusions are thus reached:

1) Both a_2 and a_3 are statistically identical. On the other hand, from equation (1) and from the definition of x , it can be deduced that

$$v_0 = - \left(\frac{dm}{dt} \right)_{t=0} = 3 m_0 \alpha. \quad (6)$$

Since v_0 and α follow the same law of type (4) whose first term is identical, it follows that

$$\log b_2 = \log b_3 + \log 3 m_0. \quad (7)$$

Expression (4) yields $\log b_2 = 6.77739$, and equation (7), $\log b_2 = 6.77729$.

This result indirectly confirms equation (1).

2) The activation energy E_1 calculated from the average of a_2 and a_3 amounts to 38373 ± 1940 cal. This value is in good agreement with the results of other authors.

Table I.*

i	y_i	a_i	$\log b_i$	r_i	$I \log y_i$	$I a_i$	$I \log b_i$
1.....	t_F	+ 9 086	— 5,566 9	0,998 84	$\pm 0,029 9$	± 275	$\pm 0,246 8$
2.....	v_0	— 8 362	+ 6,777 4	0,998 99	$\pm 0,033 3$	± 441	$\pm 0,393 7$
3.....	α	— 8 410	+ 5,030 2	0,998 15	$\pm 0,038 4$	± 510	$\pm 0,455 4$
4.....	$ \beta $	—17 030	+10,036 4	0,996 63	$\pm 0,105 4$	$\pm 1 395$	$\pm 1,244 1$
5.....	γ	—26 806	+16,110 5	0,998 77	$\pm 0,099 8$	$\pm 1 325$	$\pm 1,181 5$
6.....	A	— 553	+ 3,414 7	0,999 61	$\pm 0,001 5$	± 21	$\pm 0,018 7$
7.....	B	—22 307	+18,481 4	0,999 33	$\pm 0,082 7$	$\pm 1 129$	$\pm 1,009 9$
8.....	C	—27 710	+21,062 8	0,999 33	$\pm 0,103 0$	$\pm 1 405$	$\pm 1,256 6$

3) It is reasonable to write

$$a_4 = 2a_3, \quad \log b_4 = 2 \log b_3, \quad a_5 = 3a_3.$$

The discrepancies observed between these different values are insignificant at the probability threshold of 0.05. Similarly, one can write

$$\log b_8 = 3(1 + \varepsilon) \log b_3,$$

ε being a correction term equal to 0.067591.

Equation (1) then assumes the following form:

$$1 - \sqrt[3]{x} = b_3 e^{-\frac{E_1}{RT_0} t} - b_3^2 e^{-\frac{2E_1}{RT_0} t^2} + b_3^{3(1+\varepsilon)} e^{-\frac{3E_1}{RT_0} t^3}. \quad (8)$$

4) The final instant of decomposition t_F , root of cubic equation (1) for $x = 0$, obeying the law (5), shows that the pyrolysis follows a simple average law which, already formulated in reference 4, assumes a constant temperature Θ at all points of the cube during its decomposition:

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* Translator's Note: Commas in the table indicate decimal points.

$$1 - \sqrt[3]{x} = \frac{t}{t_F} \quad (9)$$

The first term is proportional to the time with a coefficient equal to the reciprocal of the total duration defined by equation (1). It corresponds to a decomposition rate

$$v = \frac{3}{t_F} x^{2/3} \quad (10)$$

or, replacing t_F by its value and noting that $x^{2/3} = S/S_0$ (S designates the area of the intact nucleus of calcium carbonate at instant t and S_0 its initial value)

$$v = 3b_1^{-1} e^{-\frac{E_1}{RT_0}} \frac{S}{S_0}, \quad (11)$$

in which the activation energy is

$$E_1 = 4.576 a_1.$$

Its value, $41,577 \pm 1,259$ cal, deviates significantly from that of E_1 . Equation (11) conforms to the hypothesis which we have already formulated [3].

2. Pyrolyses carried out under constant vacuum. The coefficients α , $|\beta|$, γ , $|\delta|$, η , A , $|B|$, C and the quantities t_F and v_0 rigorously obey the law (5). /332

Table II is similar to Table I and gives the same information.

Table II *

i	y_i	a_i	$\log b_i$	t_F	$\log y_i$	I_{a_i}	$I_{\log b_i}$
1.....	t_F	+ 6 570	- 5,779 5	0,997 05	$\pm 0,050 5$	± 380	$\pm 0,347 3$
2.....	v_0	- 6 365	+ 5,776 7	0,998 40	$\pm 0,038 9$	± 321	$\pm 0,293 8$
3.....	α	- 6 293	+ 3,809 6	0,998 95	$\pm 0,030 7$	± 253	$\pm 0,231 4$
4.....	$ \beta $	- 13 085	+ 8,190 5	0,997 63	$\pm 0,097 8$	± 806	$\pm 0,737 1$
5.....	γ	- 19 801	+ 12,350 2	0,997 33	$\pm 0,157 4$	$\pm 1 298$	$\pm 1,186 9$
6.....	$ \delta $	- 26 503	+ 16,284 4	0,997 35	$\pm 0,209 4$	$\pm 1 726$	$\pm 1,578 7$
7.....	η	- 33 088	+ 19,644 3	0,996 84	$\pm 0,285 4$	$\pm 2 346$	$\pm 2,140 0$
8.....	A	- 35 817	+ 23,131 4	0,998 66	$\pm 0,002 5$	± 22	$\pm 0,020 6$
9.....	$ B $	- 12 081	+ 10,586 9	0,995 84	$\pm 0,139 4$	$\pm 1 270$	$\pm 1,162 7$
10.....	C	- 18 612	+ 14,588 7	0,998 01	$\pm 0,148 2$	$\pm 1 350$	$\pm 1,236 9$

* Translator's Note: Commas in the table indicate decimal points.

Analysis of this table leads us to several conclusions.

1) It is possible to write

$$\alpha = \frac{1}{t_F},$$

$$a_1 = |a_2| = |a_3|.$$

The discrepancies observed between a_1 , $|a_2|$, and $|a_3|$ and between $|\log b_1|$ and $\log b_3$ are insignificant. It is then reasonable to take for the average a' the average of a_1 , $|a_2|$, $|a_3|$, i.e., $a' = 6409$, and for average $\log b'$ the average of $|\log b_1|$ and $\log b_3$, i.e., $\log b' = 3.7945$.

On the other hand, $\log b_3$ deduced from $\log b_2$ according to relation (7) amounts to $+4.0339$ and is slightly greater than the actual value of 3.8096 , thus showing that the theoretical curve defined by equation (2) runs slightly above the experimental curve during the first instants of pyrolysis.

2) The activation energy E of the pyrolysis of calcium carbonate carried out under constant vacuum is given by the slope a' of the straight lines representing $\log \alpha$, $\log v_0$ or $-\log t_F$ as a function of $1/T_0$. It amounts to $E_2 = 29,330 \pm 1,342$ cal. This value of E_2 , smaller than E_1 , explains the fact that at identical temperature T_0 the rate of pyrolysis is much more rapid under constant vacuum than in a stream of nitrogen.

3) It is reasonable to write

$$a_4 = 2a', \quad a_5 = 3a', \quad a_6 = 4a', \quad a_7 = 5a',$$

since the discrepancies observed between these values are not significant.

The general equation (2) then becomes

$$1 - \sqrt[3]{x} = b'e^{-\frac{E_1}{RT_0}}t - b_4e^{-\frac{2E_1}{RT_0}}t^2 + b_5e^{-\frac{3E_1}{RT_0}}t^3 - b_6e^{-\frac{4E_1}{RT_0}}t^4 + b_7e^{-\frac{5E_1}{RT_0}}t^5. \quad (12)$$

4) The equation

$$\frac{1}{t_F} = b'^{-1}e^{-\frac{E_1}{RT_0}} \quad (13)$$

leads to the same conclusions as in a stream of nitrogen: pyrolysis is carried out under constant vacuum in accordance with the law (9), and the expression for the rate v is similar to (11):

$$v = - \frac{dx}{dt} = 3b'^{-1} e^{-\frac{E_a}{RT_0}} \frac{S}{S_0}. \quad (14)$$

(General Chemistry Laboratory A, Faculty of Sciences, Avenue du Général-Leclerc, Rennes, Ille-et-Vilaine.)

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